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The results indicate that when substantial amounts of atomic hydrogen are generated at the filament, reactions of atomic hydrogen at the diamond growth surface have a pronounced effect on the substrate temperature. Use of carbon filaments lead to significantly diminished atomic hydrogen generation rates and much lower substrate temperatures. Additions of small amounts of methane to hydrogen also resulted in reduced atomic hydrogen generation rates and, consequently, lower substrate temperatures.

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HYDROGEN ASSISTED HEAT TRANSFER DURING DIAMOND GROWTH USING CARBON AND TANTALUM FILAMENTS

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ABSTRACT

Much of the previous work on the role of atomic hydrogen in diamond growth has been focussed on its formation on various refractory metal filaments, its reaction in the gas phase and its role in the growth mechanism. In contrast, the effect of atomic hydrogen recombination on substrate heating is addressed in this paper. Experiments were conducted in vacuum, helium and hydrogen environments. Tantalum and carbon filaments were used to vary atomic hydrogen generation rates. Furthermore, methane was added in some experiments to determine its effect on hydrogen assisted "chemical" heating the substrate.

The results indicate that when substantial amounts of atomic hydrogen are generated at the filament, reactions of atomic hydrogen at the diamond growth surface have a pronounced effect on the substrate temperature. Use of carbon filaments lead to significantly diminished atomic hydrogen generation rates and much lower substrate temperatures. Additions of small amounts of methane to hydrogen also resulted in reduced atomic hydrogen generation rates and, consequently, lower substrate temperatures.

In most diamond deposition techniques, atomic hydrogen is generated in significant amounts in the reactor. Various roles have been assigned to atomic hydrogen. These include selective etching of graphitic deposits[1] and stabilization of the sp^3 bonds necessary for the formation of diamond[2]. It has been suggested that hydrogen is useful both in achieving high diamond growth rates and in reducing graphitic deposits. Atomic hydrogen also reacts with hydrocarbons to form species such as CH_3 and C_2H_2 which are considered important for diamond deposition[3,4].

The formation of atomic hydrogen at the filament surface is highly endothermic. On the other hand, atomic hydrogen readily recombines on solid surfaces to form molecular hydrogen and the recombination reaction is highly exothermic. Thus, atomic hydrogen can act as a carrier of heat from the filament to the growth surface. Hydrogen assisted filament to substrate heat transfer is also potentially important in establishing spatial variations of substrate temperature and growth morphology. Atomic hydrogen concentrations have been measured by various techniques such as the multiphoton ionization[5], the laser induced fluorescence[6], mass spectroscopy[7-9] and catalytic probes[10]. Much of the work was undertaken to develop better understanding of the gas phase chemistry, gas-surface reactions and the growth mechanism. However, the role of atomic hydrogen in affecting the substrate temperature has not been investigated.

To understand the role of atomic hydrogen in heat transfer, experiments were conducted to measure the substrate temperature in specially designed hot filament diamond deposition reactors. Tantalum or carbon rod filaments were heated electrically to 2350 °C in a typical bell jar reactor. The experimental set-up is described in detail in a recent paper[11]. Silicon substrates were placed on narrow alumina supports such that the distance between the filaments and the substrate was about 8 to 9 mm. The substrate temperature was measured at its back side with a single wavelength disappearing filament optical pyrometer. The extent of substrate heating in vacuum, helium and hydrogen was determined. To study the influence of the spatial variation of atomic hydrogen concentration on the substrate temperature, a specially designed experimental set-up, shown in Figure 1, was used. An inductively heated tantalum ring filament was positioned inside a 50 mm diameter quartz reaction tube. The probe consisted of a thermocouple tip covered with a quartz thimble. The quartz thimble

served as a small substrate and provided a surface for atomic hydrogen recombination. The temperature of the probe at various locations along the axis of the reactor was recorded. Temperature measurements were made in hydrogen, helium and 1% CH_4-H_2 gas mixture for a filament temperature of 2200 °C, a reactor pressure of 30 torr and a gas flow rate of 200 sccm.

Figure 2 shows the power consumption of a tantalum filament heated to 2350 °C in vacuum, and ultra high purity helium and hydrogen in the bell jar reactor. The corresponding substrate temperatures measured using the optical pyrometer are also presented. The results indicate that the power requirements were almost equal in vacuum and helium environments. Furthermore, the difference in the substrate temperatures was insignificant. However, in hydrogen both the filament power consumption and the substrate temperature were substantially higher than the corresponding values in the other environments.

At steady state, the power consumption by the filament is equal to the combined effects of heat loss by convection, conduction and radiation, and the energy absorption by the endothermic reactions at the filament surface. Since there are no conduction and convection heat losses in vacuum, the power consumed to heat the filament to a given temperature is equal to radiative heat loss from the filament. The power consumption in helium is indicative of the heat losses due to conduction and convection in addition to radiation. The small increase in the power requirement when helium is introduced in the vacuum chamber indicates that conductive and convective heat losses from the filament are small compared to the radiative heat loss under typical hot filament assisted diamond deposition conditions. The substrate temperature in vacuum was less than the minimum detectable, about 700 °C, and did not appear to increase when the filament was heated in helium instead of vacuum. These results indicate that conductive and convective heat transfer to the substrate are negligible compared to radiative heat transfer.

The substrate temperature in hydrogen was significantly higher than that in helium under identical conditions of filament temperature, reactor pressure and gas flow rate. Since the rate of heat transfer from the filament to the substrate by conduction, convection and radiation is roughly equal in helium and hydrogen, the results indi

cate an additional important mechanism of heat transport in hydrogen environment. When the filament is heated to temperatures in excess of 2000 °C at low pressures, significant amount of atomic hydrogen is generated at the filament surface. The observation that the power required to heat the filament to a desired temperature in hydrogen was higher than that in helium is consistent with endothermic dissociation of hydrogen at the filament surface[12]. The atomic hydrogen generated at the filament is transported to the substrate primarily by diffusion[13,14]. Furthermore, previous investigations[14,15] have shown that homogeneous chemical reactions in the gas phase do not significantly alter the atomic hydrogen concentration indicating that a significant proportion of the atomic hydrogen generated at the filament reaches the substrate surface. In the presence of a solid surface, atomic hydrogen readily recombines to form molecular hydrogen.

$$H + H = H_2 \quad \Delta H^{\circ} = -104 \text{ kcal/mole of } H_2 \tag{1}$$

This recombination is highly exothermic and the energy released heats the substrate. Thus, the endothermic generation of atomic hydrogen at the filament and its subsequent transport to the growth surface, where it recombines to form molecular hydrogen, serves as an additional mechanism of heat transport to the substrate. A steady flux of atomic hydrogen aids in providing a continuous source of heat to the substrate and the substrate temperature rises. However, since the radiation heat loss from the substrate is proportional to the fourth power of temperature, a steady state is reached rapidly. The heat input to the substrate is balanced by the heat lost by radiation, conduction and convection. At a filament to substrate distance of about 1 cm, the substrate temperature was at least 250 °C higher in hydrogen than in helium. Thus, in typical hot filament systems where the substrate is placed about 3 to 10 mm away from the filament, atomic hydrogen recombination plays a major role in substrate heating.

Several experiments were conducted with carbon filaments to confirm that the enhanced heating of the substrate in hydrogen was primarily due to atomic hydrogen recombination. If the atomic hydrogen generation rate at the filament is diminished, the flux and hence the recombination rate of atomic hydrogen at the substrate will also be diminished. Thus, if a change in the atomic hydrogen generation rate brings

about a corresponding change in the substrate temperature, the observed effect can be attributed to atomic hydrogen recombination. The presence of carbon at the filament surface suppresses the generation of atomic hydrogen at the filament[16,17]. Carbon filaments were heated to 2350 °C at 30 torr and a gas flow rate of 200 sccm. The power consumed by the filamr , in different atmospheres and the corresponding substrate temperatures are presented in Figure 3. Once again, it is observed from the measurements of filament power consumption and substrate temperature in vacuum and helium that heat transfer by convection and conduction are negligible compared to radiative heat transfer. When a carbon filament was used, the power requirement in hydrogen was only slightly higher than that in helium. This suggests that a relatively small amount of atomic hydrogen is generated at the surface of the carbon filament. Furthermore, the substrate temperature in hydrogen was not very different from that in helium. Thus, atomic hydrogen plays a major role in heating the substrate only when present in substantial amounts. When carbon filaments are used and the concentration of atomic hydrogen is low, substrate heating occurs primarily by radiation. Diamond deposition has been achieved using carbon elements, albiet at relatively low growth rates. The details of diamond growth using carbon filaments are available elsewhere[18].

Experiments were carried out to study the effects of the spatial variation of atomic hydrogen concentration on the substrate temperature. Figure 4 shows the variation of probe temperature with distance along the axis of the reactor in ultra high purity helium, hydrogen and a mixture of 1% methane in hydrogen. At any monitoring location, the temperature in helium was significantly lower than that in either pure hydrogen or in 1% CH_4-H_2 mixture. In each case, the temperature decreased rapidly with distance from the filament. However, the decrease in temperature was much more pronounced in hydrogen than in helium, indicating that the extent of substrate heating is affected by the local concentration of atomic hydrogen. Thus, in hot filament assisted deposition, the spatial variation of atomic hydrogen can influence substrate temperature uniformity and resulting film properties.

The power required to heat the filament in a methane-hydrogen mixture was lower than that required in pure hydrogen. Furthermore, the addition of a small amount of methane to hydrogen resulted in a lowering of the thermocouple temperature. Addi-

tion of methane is known to lower the efficiency of generation of atomic hydrogen at the filament[16,17]. If the generation of atomic hydrogen is reduced due to the addition of methane and the homogeneous reactions of atomic hydrogen do not change the concentration by any appreciable amount, the shapes of the atomic hydrogen concentration profiles in hydrogen and 1% CH_4-H_2 should be nearly identical. It is observed from Figure 4 that the shape of the experimentally determined temperature profile in 1% CH_4-H_2 is nearly identical to that in pure hydrogen. It has been demonstrated before that the probe temperature is significantly affected by the concentration of atomic hydrogen. Thus, the observed decrease in probe temperature is consistent with the decrease in the concentration of atomic hydrogen at the filament when methane is introduced in the reactor.

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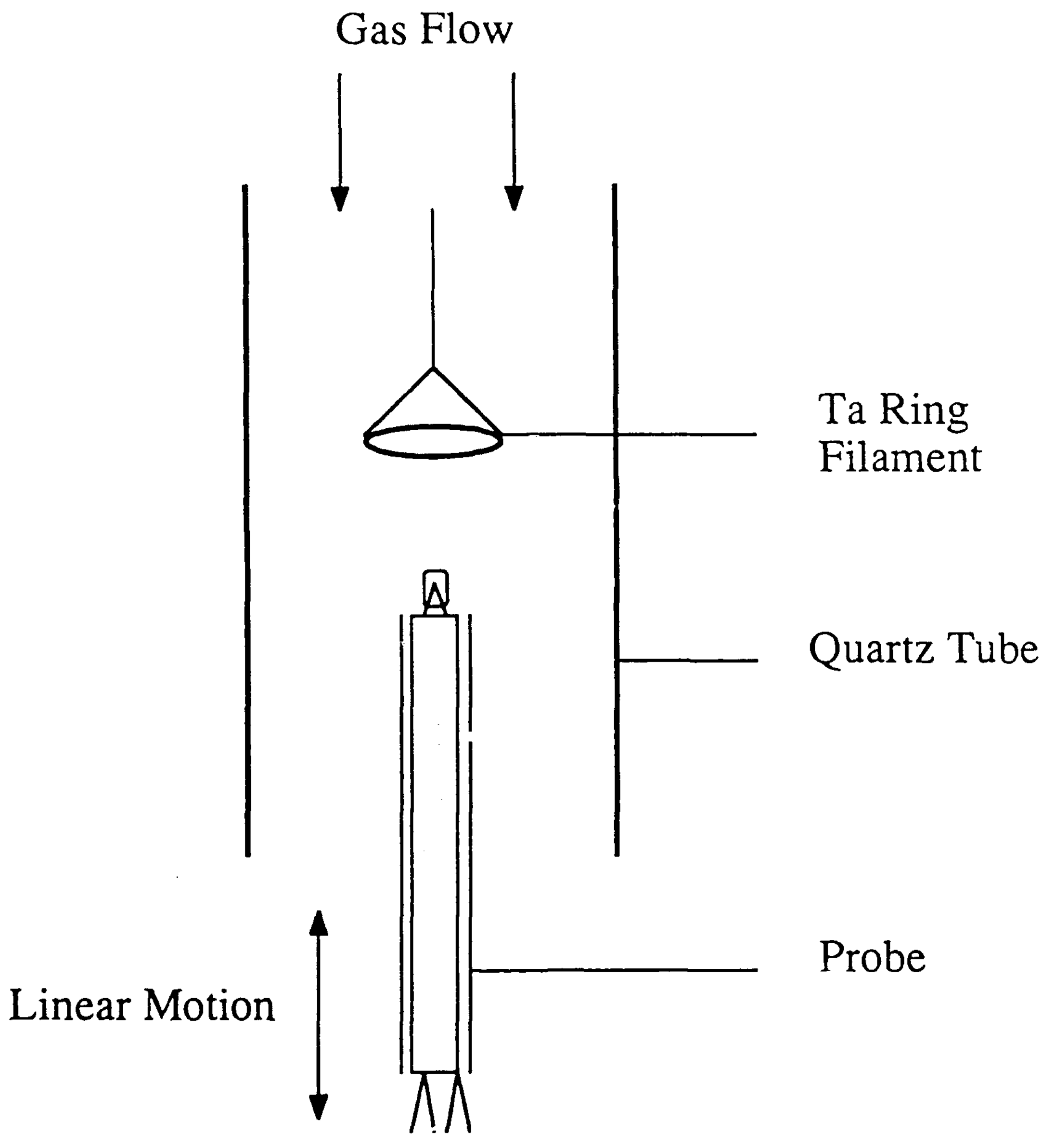
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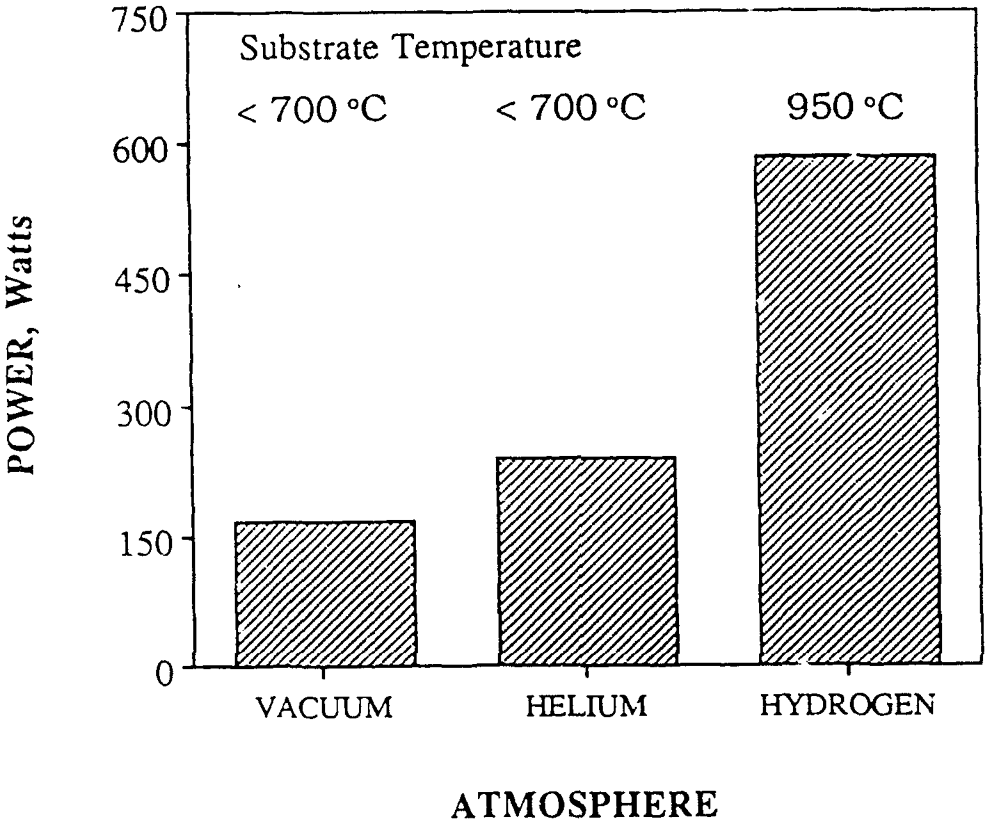
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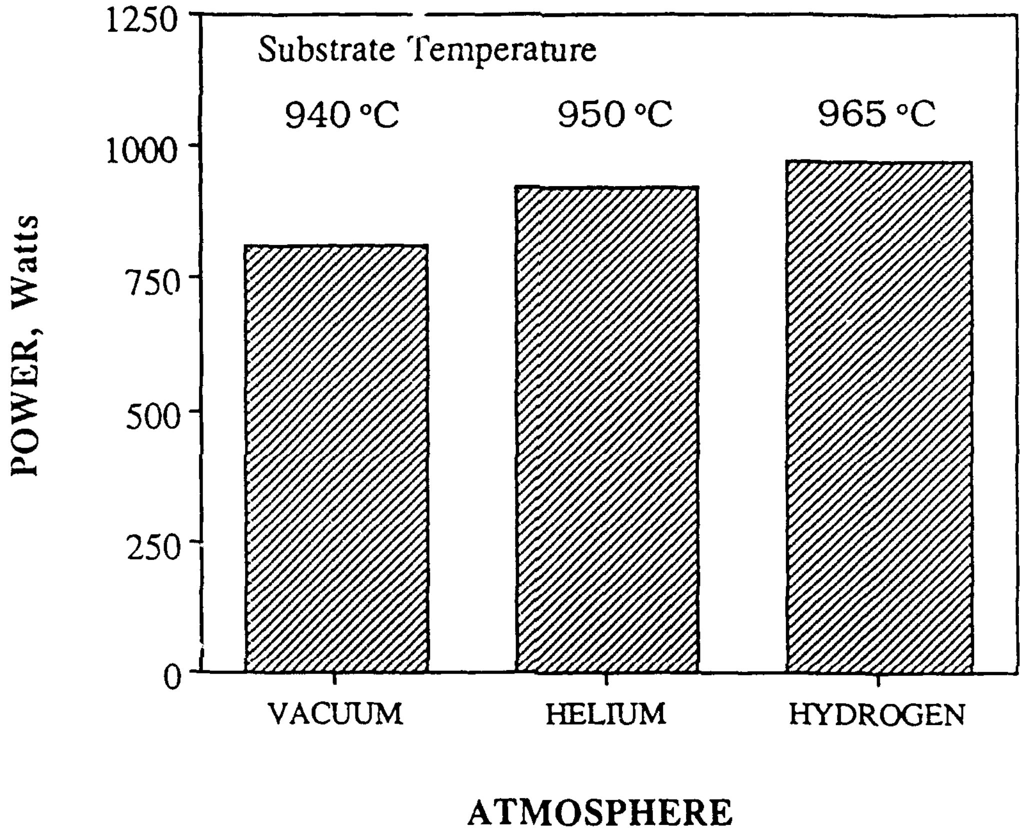

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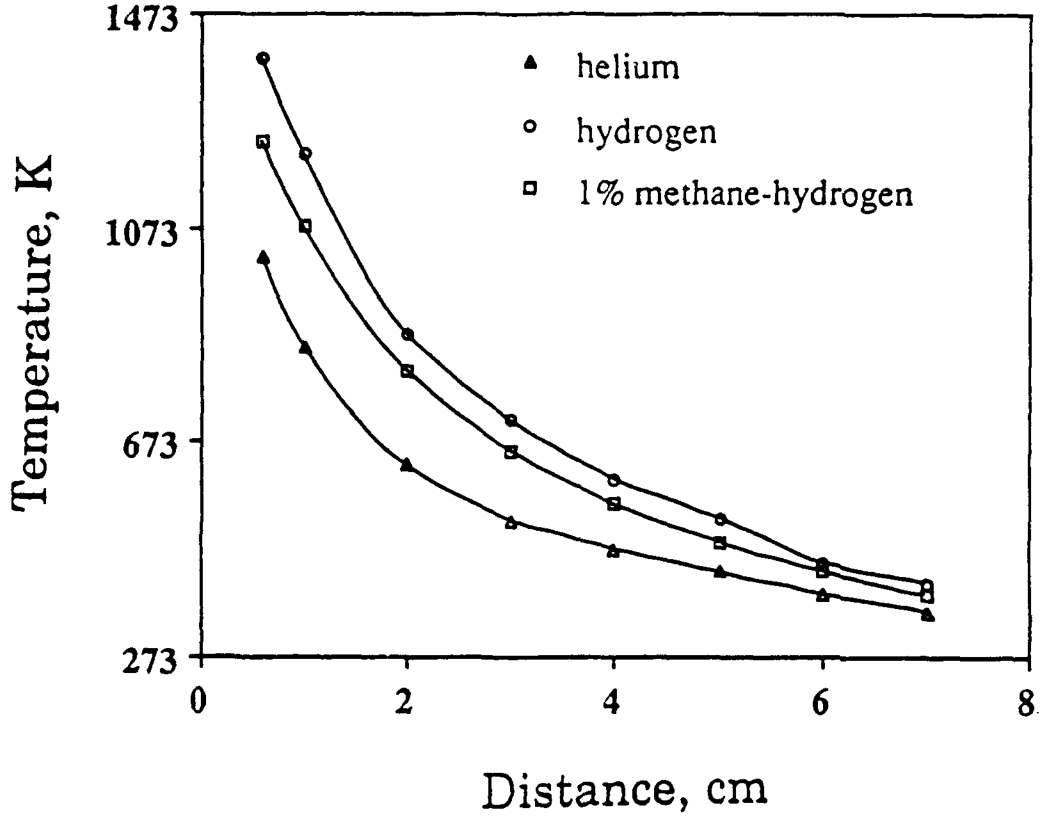
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